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<b>(54) Title:</b> MELT PROCESS FORMATION OF POLYMER NANOCOMPOSITE OF EXFOLIATED LAYERED MATERIAL  <b>(57) Abstract</b>  This invention relates to a process of forming a polymeric nanocomposite comprising a continuous polymeric phase formed from a melt processible polymer and platelet particles having an average thickness equal to or less than about 50 Å, and the polymeric nanocomposite formed by said process.		

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MELT PROCESS FORMATION OF POLYMER NANOCOMPOSITE  
OF EXFOLIATED LAYERED MATERIAL

5    1.   Field of the Invention

          This invention relates to a process for forming a composite material comprising a polymer matrix having dispersed therein platelet particles, derived from swellable intercalated layered materials, and to  
10   composite material formed by the process of this invention. More particularly, this invention relates to such a process where the intercalated layered material has layers which are compatible with the polymer of the matrix, such that during the process the  
15   polymer-compatible layers of the intercalated material dissociate one from the other to form platelet fillers.

          2.   Prior Art

          A specific category of polymer nanocomposites has  
20   been described as a composite material comprising a polymer matrix containing a polyamide having uniformly dispersed therein layers of silicate. Such nanocomposites are described in US Pat No. 4,739,007 and No. 4,810,734, Deutsches Pat. 3808623 A1, Japanese  
25   Patent J 02 208358 A, and technical publications by the patentees (J. Inclusion Phenomena 5, (1987), 473-483; Clay Minerals, 23, (1988), 27; Polym. Preprints, 32, (April 1991), 65-66; and Polym. Prints, 28, (August 1987), 447-448.

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SUMMARY OF THE INVENTION

          This invention relates to a process for forming a polymeric composite which comprises platelet particles dispersed in a polymeric matrix which comprises the  
35   steps of:

          (a) forming a "flowable mixture" comprising a melt-processible polymer and a swellable and polymer-

compatible intercalated layered material having layers that are compatible with said polymer; and

(b) subjecting said mixture to a shear having a shear rate which is sufficient to dissociate all or a portion of said layers one from the other to form platelet particles having an average thickness equal to or less than about 50 Å, and preferably having a maximum thickness of 100 Å, and to uniformly disperse said platelet particles in said polymer to form said polymer composite.

Another aspect of this invention relates to a composite material comprising a polymeric matrix which comprises a melt processible polymer having uniformly dispersed therein platelet particles having an average thickness equal to or less than about 50 Å and preferably having a maximum thickness equal to or less than about 100 Å, said platelets having a chemical species bonded to the surface thereof and which is not covalently bonded to said polymer. The process is directed toward preparation of polymer composites wherein the dispersed phase comprises platelet particles having two flat opposite faces, the thickness of which particles is the distance between these faces. The thickness is relatively small compared to the size of the flat opposite faces. Dispersing such finely divided platelet particles imparts a very large area of contact between polymer and particles for a given volume of particles in the composite and a high degree of homogeneity of the composite with respect to the particular effect of the dispersed particles. Platelet particles of high strength and modulus, dispersed at sub-micron size (nanoscale), impart greater mechanical reinforcement to the polymer matrix than do comparable loadings of conventional reinforcing fillers of micron size. Nanoscale barrier layers impart lower permeability to polymers than do comparable loadings of conventional barrier fillers.

The process of this invention exhibits several advantages over monomer blending and polymerizing processes of the type described in U.S. Patent Nos. 4,810,734 and 4,739,007, also referred to herein as in-reactor processes. These advantages include utility for a broader range of matrix polymers; utility for a wider range of composites having the same matrix polymer due to a larger selection of swelling/compatibilizing agents, each having a distinct bonding interaction with both the polymer and the platelet particle; and greater control over the molecular weight distribution of the matrix polymer. For example, virtually any polymer material that can be made to flow can be compounded with nanoscale particles derived from intercalated layered materials which exfoliate during mixing in accordance with the process of this invention. In contrast, the monomer blending and polymerizing processes of the prior art are restricted to polymers whose monomers are compatible with layered materials and can be polymerized effectively in the presence of the layered material. In the process of the present invention, the compounding entails no special conditions specific to selected polymer molecular weight distributions. On the other hand, in-reactor processes of the prior art require special polymerization conditions for each selected molecular weight distribution due to the effect of a dispersed phase on reaction mixture viscosity and polymerization kinetics. Virtually any loading of intercalated layered material is possible in the process of this invention, whereas in-reactor compounding of the prior art processes may be practically limited to loadings that permit polymerization to proceed to a selected molecular weight.

Another advantage is that compatibilizing agents including silane coupling agents can be readily used in

the process of this invention. These coupling agents can bond to the platelet particles through water- and chemical-resistant covalent bonds such as M-O-Si-C bonds, where M is a metal such as Si, Mg and Al. They can then couple the particles to the matrix polymer and other polymers via a variety of bonding interactions including covalent bonds, hydrogen-bonds, dipole-dipole bonds and interchain entanglement. Some of these silane coupling agents can not be used in monomer blending and polymerizing processes of the prior art. For example, silane coupling agents may hydrolyse or decompose under the polymerization conditions described in U.S. Patent Nos. 4,739,007 and 4,810,734. Specifically layered materials intercalated by swelling/compatibilizing agents which are compounded in the in-reactor blending processes of the prior art must survive polymerization conditions (e.g., several hours in water vapor at 250°C, or 30 minutes in strong reducing agents at 180°C, in the case of caprolactam polymerization by cationic and anionic processes, respectively). In contrast, only short high temperature exposures are required for the present process, such as about 1 minute at 250°C for compounding layered materials with nylon 6 to form a nanocomposite.

As a further advantage of the present process, unreacted monomer can be removed prior to forming the nanocomposite. This facilitates monomer removal, for example by solvent extraction, since dispersed particles can interfere with this process.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more fully understood and further advantages of the invention will become apparent when reference is made to the following detailed description of the invention and accompanying drawings in which:

FIG 1 is a graph of elastic modulus versus temperature for a nylon 6/montmorillonite nanocomposite.

FIG 2 is a graph of elastic modulus versus temperature for a nylon 6/montmorillonite nanocomposite and for a composite of nylon 6 with unintercalated montmorillonite.

FIG 3 is a micrograph of the extruded nanocomposite formed by the process of this invention of Example 3 obtained by transmission electron microscopy.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**  
**OF THE INVENTION**

The first step of this invention comprises forming a "flowable mixture" comprising one or more polymers in a "polymer melt" and at least one "swellable and polymer-compatible intercalated layered material" which comprises polymer-compatible layers that are compatible with said polymers. As used herein, a "flowable mixture" is a mixture which is capable of flowing at the submicron scale so that the layered materials may exfoliate into platelet particles comprising individual or a small multiple of layers, which may in turn disperse within the polymer mixture. As used herein, a "polymer melt" is a melt processible polymer or mixture of polymers which has been heated to a temperature sufficiently high to produce a viscosity low enough for submicron scale mixing to occur. Temperatures used in the first step are not critical and can be varied widely as desired provided that the polymer employed is in the state of a polymer melt. In the preferred embodiments of the invention, process temperature should be at least as high as the melting point of the particular polymer employed, and below the degradation temperature of the polymer. In the more preferred embodiments of this invention, where the polymer is a thermoplastic polymer, the process temperature is such

that the polymer will remain in the polymer melt during the conduct of the process. In the case of a crystalline thermoplastic polymers, the temperature is above the polymer's melting temperature. For example, a typical nylon 6 having a melting point of about 225°C can be melted in an extruder at any temperature equal to or greater than about 225°C, as for example between about 225°C and about 325°C. For nylon 6, a temperature of preferably from about 250°C to about 260°C is normally employed. In the cases of amorphous thermoplastics and vulcanizable rubbers, it is a temperature at which the viscosity is sufficiently low that processing of the polymer can be performed by conventional means.

The manner in which the flowable mixture is formed is not critical and conventional methods can be employed. For example, the flowable mixture can be prepared through use of conventional polymer and additive blending means, in which the polymer is heated to a temperature sufficient to form a polymer melt and combined with the desired amount of the intercalated layered material in a granulated or powdered form in a suitable mixer, as for example an extruder, a Banbury Mixer, a Brabender mixer, a continuous mixer and the like. The polymer melt containing nano-dispersed delaminated layered material may also be formed by reactive extrusion in which the layered material is initially dispersed as aggregates or at the nanoscale in a liquid or solid monomer and this monomer is subsequently polymerized in an extruder or the like. Such monomer or other reactive solid or liquid dispersion can be injected into a polymer melt containing one or more polymers in an extruder or other mixing device. The injected liquid may result in new polymer or in chain extension or grafting to the polymer initially in the melt. Alternatively, the polymer may be granulated and dry mixed with the

intercalated layered material, and thereafter, the composition may be heated in a mixer until the polymer is melted forming the flowable mixture. As described above, the flowable mixture is, in the second step, 5 subjected to a shear in a mixer sufficient to form the dispersed nanocomposite structure of platelet particles in the polymer melt, and it is thereafter cooled.

Best results are generally obtained when the flowable mixture includes as little water as possible 10 in order to avoid hydrolytic cleavage of the polymer and/or generation of void defects. Some polymers such as polyolefins can tolerate more than about 0.25% water by weight during melt processing, while others (such as condensation polymers as for example polyamides and 15 polyesters) may be degraded if processed with water content greater than about 0.1% by weight. Consequently, in the most preferred embodiments, both the polymer and the intercalated layered material are rigorously dried and contain substantially no water. 20 Ideally, the intercalated layered material is free of water that can be desorbed at temperatures up to the processing temperature. However, good results can be obtained when the intercalated layered material contains as much as about 2% by weight water and 25 comprises less than about 5% by weight of the flowable mixture. For compounding with condensation polymers, the intercalated layered material preferably contains less than about 1% by weight, more preferably less than about 0.5% by weight water and most preferably 30 less than about 0.25% by weight water.

As a first essential ingredient, the flowable mixture includes a "swellable and polymer-compatible intercalated material". As used herein, a "swellable and polymer-compatible intercalated layered material" 35 is a swellable layered material intercalated by a neutral or ionic intercalant or intercalants which act to weaken the interlayer cohesive energy by swelling

the interlayer distances. In the preferred embodiments of the invention, the intercalant or intercalants increase the compatibility and bonding of the layers with the polymer melt by having attractive interactions with both the layers and the polymer. Intercalants which function to swell interlayer distances are hereinafter referred to as "swelling agents", intercalants which function to increase the compatibility and bonding of the layers with the polymer melt are hereinafter referred to as "compatibilizing agents" and intercalants which function as swelling agents and compatibilizing agents are hereinafter referred to as "swelling/compatibilizing agents".

Swellable layered materials are materials comprising planar layers arrayed in a coherent, coplanar structure, where the bonding within the layers, is stronger than the bonding between the layers such that the materials exhibit increased interlayer spacing in their intercalation compounds. The neutral or ionic molecules, called "intercalants", may be introduced into the interlayer spaces by either insertion, in the case of neutral molecules, or ion exchange, in the case of ions. The intercalants may be introduced in the form of a solid, liquid, gas, or solute. The intercalants may be introduced into the spaces between every layer, nearly every layer, or a large fraction of the layers of the layered material such that the resulting platelet particles comprise less than about 10 layers in thickness. The platelet particles are preferably less than about 8 layers in thickness, more preferably less than about 5 layers in thickness, and most preferably, about 1 or 2 layers in thickness.

Any swellable layered material having the above referenced characteristics may be used in the practice of this invention. Useful swellable layered materials

include phyllosilicates. Illustrative of such materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite, magadiite, and kenyaite; vermiculite; and the like. Other useful layered materials include illite minerals such as ledikite and admixtures of illites with the clay minerals named above. Other useful layered materials, particularly useful with anionic polymers, are the layered double hydroxides, such as  $\text{Mg}_6\text{Al}_{3.4}(\text{OH})_{18.8}(\text{CO}_3)_{1.7}\text{H}_2\text{O}$  (see W.T. Reichle, J. Catal., 94 (12985) 547), which have positively charged layers and exchangeable anions in the interlayer spaces. Other layered materials having little or no charge on the layers may be useful in this invention provided they can be intercalated with swelling agents which expand their interlayer spacing. Such materials include chlorides such as  $\text{ReCl}_3$  and  $\text{FeOCl}$ , chalcogenides such as  $\text{TiS}_2$ ,  $\text{MoS}_2$ , and  $\text{MoS}_3$ , cyanides such as  $\text{Ni}(\text{CN})_2$ , and oxides such as  $\text{H}_2\text{Si}_2\text{O}_5$ ,  $\text{V}_6\text{O}_{13}$ ,  $\text{HTiNbO}_5$ ,  $\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$ ,  $\text{W}_{0.2}\text{V}_{2.8}\text{O}_7$ ,  $\text{Cr}_3\text{O}_8$ ,  $\text{MoO}_3(\text{OH})_2$ ,  $\text{VOPO}_4\cdot 2\text{H}_2\text{O}$ ,  $\text{CaPO}_4\text{CH}_3\cdot \text{H}_2\text{O}$ ,  $\text{MnHAsO}_4\cdot \text{H}_2\text{O}$ ,  $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ , and the like. Preferred swellable layered materials are phyllosilicates of the 2:1 type having a negative charge on the layers ranging from about 0.25 to about 0.9 charges per formula unit and a commensurate number of exchangeable cations in the interlayer spaces. Most preferred layered materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite, magadiite, and kenyaite.

Swellable layered materials, such as the preferred smectite clay materials generally require treatment by one or more intercalants to provide the required interlayer swelling and/or polymer compatibility. The resulting interlayer spacing is critical to the performance of the intercalated layered material in the practice of this invention. As used herein the "inter-

layer spacing" refers to the distance between the faces of the layers as they are assembled in the intercalated material before any delamination (or exfoliation) takes place. The preferred clay materials generally include interlayer or exchangeable cations such as  $\text{Na}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$  and the like. In this state, these materials do not delaminate in host polymer melts regardless of mixing, because their interlayer spacings are usually equal to or less than about 4 Å consequently the interlayer cohesive energy is relatively strong. Moreover, the metal cations do not aid compatibility between layers and the polymer melt. In the preferred embodiments, these layered materials are intercalated by swelling agents of sufficient size to increase interlayer distances to the desired extent. In general, the interlayer distance should be at least about 4 Å, as determined by x-ray diffraction, in order to facilitate delamination of the layered material at the nanoscale. In the preferred embodiments of the invention, the interlayer distance is at least about 8 Å and more preferred interlayer distances are at least about 15 Å. In these preferred embodiments, the swelling agent is an ionic species which is capable of exchanging with the interlayer cations such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ , and  $\text{Ca}^{+2}$  and is of sufficient size to provide the required interlayer distance. Such ionic species include  $\text{NH}_4^+$ ,  $\text{Al}^{+3}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{+3}$ ,  $\text{NH}_2\text{R}^1$ ,  $\text{NH}_2\text{R}^1\text{R}^{2+}$ ,  $\text{NHR}^1\text{R}^2\text{R}^3$ ,  $\text{NR}^1\text{R}^2\text{R}^3\text{R}^4$ , where the  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are the same or different and are organic substituents, and the like.

In order to further facilitate delamination of layered materials into platelet particles and prevent reaggregation of the particles, these layers are preferably polymer-compatible. In cases where the polymer melt is not compatible with the layers, the swellable layered material is intercalated by compatibilizing agents which consist of a portion which

bonds to the surface of the layers and another portion which bonds or interacts favorably with the polymer. In some instances, intercalants are used which are swelling/compatibilizing agents which provide both the swelling function and the compatibilization function. Such agents preferably include a moiety or moieties which interact with the surface of the layers displacing, totally or in part, the original metal ions and which bonds to the surface of the layers; and includes a moiety or moieties whose cohesive energies are sufficiently similar to that of the polymer that the surface of the platelets is made more compatible with the polymer, thereby enhancing the homogeneity of the dispersion in the polymeric matrix. As used herein "compatible" refers to the extent to which the polymer matrix and the surface coating on the platelet particles (the compatibilizing agent) have a favorable interaction which promotes the intermingling of the matrix polymer and the surface layer in the interphase region. Compatibility derives from one or more of the following criteria: similar cohesive energy densities for the polymer and the derivatized platelets, similar or complimentary capacities for dispersive, polar, or hydrogen bonding interactions, or other specific interactions, such as acid/base or Lewis-acid/Lewis-base interactions. Compatibilization will lead to an improved dispersion of the platelet particles in the matrix and an improved percentage of delaminated platelets with a thickness of less than 50 Å.

The nature of the swelling/compatibilizing agent, swelling agent and/or compatibilizing agent will vary widely depending on the particular polymer and the particular layered material. For example, where the swellable layered material is a phyllosilicate as for example a smectite clay and the polymer is a polyolefin, polyester or polyamide such as polyethylene, polypropylene, poly(caprolactam) and

poly(ethylene terephthalate), swelling/compatibilizing agents are preferably zwitterionic and cationic surfactant type molecules, and most preferably cationic surfactant type materials. Useful cationic surfactants include onium species such as ammonium (primary, secondary, tertiary, and quaternary), phosphonium or sulfonium derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines and sulfides. Illustrative of such materials are oxonium compounds of the formula:



where  $X^+$  is an ammonium, sulfonium or phosphonium radical such as  $-NH_3^+$ ,  $-N(CH_3)_3^+$ ,  $-N(CH_3)_2(CH_2CH_3)^+$ ,  $+S(CH_3)_3$ ,  $-^+P(CH_3)_3$ ,  $-NH_4^+$  (where  $R^5$  is  $-(CH_2)_n$ ), and the like and  $R^5$  is an organic radical as for example substituted or unsubstituted alkyl, cycloalkenyl, cycloalkyl, aryl, or alkylaryl, either unsubstituted or substituted with amino, alkylamino, dialkylamino, nitro, azido, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, alkyl, aryloxy, arylalkylamino, alkylamino, arylamino, dialkylamino, diarylamino, aryl, alkylsulfinyl, aryloxy, alkylsulfinyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, alkylsilane, and a moiety of the formula:



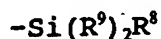
wherein  $R^6$  is alkyl, cycloalkyl, aryl,  $R'$  is hydrogen, alkyl, or aryl, and  $Z$  is  $-O-$  or  $-NR^7-$ , where  $R^7$  is hydrogen, alkyl, aryl or alkylsilane. Illustrative of useful  $R^5$  groups are hydrogen, alkyl, such as methyl, ethyl, octyl, nonyl, tert-butyl, neopentyl, isopropyl, sec-butyl, dodecyl and the like; alkenyl such as 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl and the like; alkoxy such as

propoxy, butoxy, methoxy, isopropoxy, pentoxy, nonoxy, ethoxy, octoxy, and the like; cycloalkenyl such as cyclohexenyl, cyclopentenyl and the like; alkanoylalkyl such as butanoyl octadecyl, pentanoyl nonadecyl, 5 octanoyl pentadecyl, ethanoyl undecyl, propanoyl hexadecyl and the like; amino; alkylaminoalkyl, such as methylamino octadecyl, ethylamino pentadecyl, butylamino nonadecyl and the like; dialkylaminoalkyl, such as dimethylamino octadecyl, methylethylamino 10 nonadecyl and the like; arylaminoalkyl such as phenylamino octadecyl, p-methylphenylamino nonadecyl and the like; diarylaminoalkyl, such as diphenylamino pentadecyl, p-nitrophenyl-p'-methylphenylamino octadecyl and the like; alkylarylaminomalkyl, such as 15 2-phenyl-4-methylamino pentadecyl and the like; alkylsulfinyl, alkylsulfonyl, alkylthio, arylthio, arylsulfinyl, and arylsulfonyl such as butylthio octadecyl, neopentylthio pentadecyl, methylsulfinyl nonadecyl, benzylsulfinyl pentadecyl, phenylsulfinyl 20 octadecyl, propylthiooctadecyl, octylthio pentadecyl, nonylsulfonyl nonadecyl, octylsulfonyl hexadecyl, methylthio nonadecyl, isopropylthio octadecyl, phenylsulfonyl pentadecyl, methylsulfonyl nonadecyl, nonylthio pentadecyl, phenylthio octadecyl, ethylthio 25 nonadecyl, benzylthio undecyl, phenethylthio pentadecyl, sec-butylthio octadecyl, naphthylthio undecyl and the like; alkoxycarbonylalkyl such as methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl and the like; cycloalkyl such as cyclohexyl, cyclopentyl, 30 cyclo-octyl, cycloheptyl and the like; alkoxyalkyl such as methoxy-methyl, ethoxymethyl, butoxymethyl, propoxyethyl, pentoxybutyl and the like; aryloxyalkyl and aryloxyaryl such as phenoxyphenyl, phenoxymethyl and the like; aryloryalkyl such as phenoxydecyl, 35 phenoxyoctyl and the like; arylalkyl such as benzyl, phenethyl, 8-phenyloctyl, 10-phenyldecyl and the like; alkylaryl such as 3-decylphenyl, 4-octylphenyl, 4-

nonylphenyl and the like; and polypropylene glycol and polyethylene glycol substituents such as ethyl, propyl, butyl, phenyl, benzyl, tolyl, p-styryl, p-phenylmethyl chloride, octyl, dodecyl, octadecyl, methoxy-ethyl, 5 moieties of the formula  $-C_3H_6COOH$ ,  $-C_5H_{10}COOH$ ,  $-C_7H_{10}COOH$ ,  $-C_7H_{14}COOH$ ,  $-C_9H_{18}COOH$ ,  $-C_{11}H_{22}COOH$ ,  $-C_{13}H_{26}COOH$ ,  $-C_{15}H_{30}COOH$  and  $-C_{17}H_{34}COOH$  and  $CH=C(CH_3)COOCH_2CH_2-$ , and the like. Such ammonium, sulfonium and phosphonium radicals are well known in the art and can be derived from the 10 corresponding amines, phosphines, and sulfides.

Useful swelling/compatibilizing agents also include neutral compounds. For example useful swelling/compatibilizing agents include neutral amine, phosphine, and sulfide forms of the above-referenced 15 oxonium compounds which hydrogen bond to the layers. In this case, the original metal cations are not replaced.

Another class of swelling/compatibilizing agents are those which are covalently bonded to the layers. 20 Illustrative of such groups useful in the practice of this invention are silane coupling agents of the formula:



25 where  $R^9$  is the same or different at each occurrence and is alkyl, alkoxy or oxysilane such as trialkoxysilane compounds as for example octadecyltrimethoxysilane, gamma-aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, 30 gamma-aminopropylphenyldimethoxysilane, gamma-glycidoxypropyl tripropoxysilane, 3,3-epoxycyclohexylethyl trimethoxysilane, gamma-propionamido trithoxysilane, N-trimethoxysilylpropyl-N(beta-aminoethyl) amine, trimethoxysilylundecylamine, 35 trimethoxy silyl-2-chloromethylphenylethane, trimethoxysilyl-ethylphenylsulfonylazide, N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride,

N-(trimethoxysilylpropyl)-N-methyl-N,N-diallylammonium chloride, trimethoxysilylpropylcinnamate, 3-mercaptopropyl trimethoxysilane, 3-isocyanatopropyl-triethoxysilane, and the like; and R<sup>8</sup> is selected from  
5 the group consisting of organic radicals which are compatible with the polymer forming the composite.

In other instances, it is convenient to use a compatibilizing agent that is different from the swelling agent. For example, alkylammonium cations may  
10 be used to replace the metal cations of a smectite mineral, and be partially replaced, in turn, by a silane coupling agent. In this case, the alkylammonium cation functions as a general purpose swelling agent while the silane can function as a compatibilizing  
15 agent that is highly specific to a selected polymer system.

In the preferred embodiments of the invention, the swelling agent, compatibilizing agent and/or swelling/compatibilizing agent will include a moiety  
20 which bonds to the surface of the layered material and will not be reactive with the polymer. Preferably the agent will also include a moiety which does not bond with the layered material and which is compatible with the polymer. In the preferred embodiments of this  
25 invention, swelling/compatibilizing agents are employed, especially onium agents and silane agents. In the preferred embodiments of the invention lipophilic swelling and compatibilizing agents are used. Such agents will preferably include a lipophilic  
30 portion as for example a long chain alkyl, alkenyl or alkylaryl group (preferably of more than about 9 aliphatic carbon atoms). Such agents are well known in the art and include silane compounds and the ammonium, sulfonium and phosphonium derivatives of  
35 octadecylamine, octadecylphosphine, trimethyl dodecyl sulfide, octadecylsulfide, dimethyldidodecyl amine,

octadecylamine, dioctylphosphine, methyloctadecylamine, dioctylsulfine, decylsulfide and the like.

The preferred intercalated layered materials of the present art enables formation of nanocomposites with high molecular weight polymers. In such preferred cases, the polymer in the nanocomposites has substantially the same molecular weight distribution as obtained for the same polymer similarly processed in the absence of the intercalated material. In contrast, Fukushima et al. show in Clay Minerals, 23, (1988), 27 that the number average molecular weight obtained by the in-reactor process substantially decreases with increasing weight percent of the clay in nylon-6. Preferred for the present invention are nanocomposites of nylon 6 in which the number average molecular weight is about 15,000 and the ratio of weight average to number average molecular weight ( $M_w/M_n$ ) is less than 3.0. Especially preferred are those nanocomposites in which the number average molecular weight is above approximately 25,000. In contrast with these preferences, Fukushima et al., (Clay Minerals, 23, (1988), 27) teach that the  $M_n$  for in-reactor formed nylon nanocomposites decreases from 36,000 at 5.30 wt %  $\text{NH}_3^+(\text{CH}_2)_{10}\text{COOH}$ - montmorillorite loading ( $M_w/M_n=10.5$ ) to 15,000 ( $M_w/M_n=14.0$ ) at 18.2 intercalated wt% clay, and to 8,000 ( $M_w/M_n=11.7$ ) at 31.4 wt% of intercalated clay. For the purposes of this invention  $M_n$  and  $M_w$  are measured by gel permeation chromatography in m-cresol at 100°C and contributions in the distribution from unreacted caprolactam are excluded from Mn and Mw evaluations.

We surprisingly found that omega-aminoacids, the preferred swelling/compatibilizing agents of U.S. Patent Nos. 4,739,007 and 4,810,734, are not preferred as swelling/ compatibilizing agents for swellable clay minerals compounded into molten polymers. Omega-aminoacids do not separate the swellable clay mineral

layers by more than 4 Å, once the removable water has been eliminated from the intercalated layered material. Nor are omega-aminoacids lipophilic and they do not make the mineral layers hydrophobic, and cannot be easily dried prior to compounding. Thus, such aminoacid intercalated materials and other such intercalated materials which are intercalated by molecules which tend to lie flat against the layers of the silicate do not readily delaminate in the polymer melt. The resulting large particles and gels which are present in the final polymer composite lead to a reduction of mechanical strength, impact resistance and optical clarity. In contrast, swellable mineral layers swollen and compatibilized with lipophilic swelling/compatibilizing agents such as the onium salts of hydrocarbon amines, phosphines and sulfides (such as octadecylamine), and silane derivatives of hydrocarbons (such as octadecyl-trimethoxysilane) possess no hydrophilic group such as a carboxylate group which can also bond ionically or through hydrogen bonds to the silicate layers. As a result, the lipophilic agents provide interlayer spacings of more than about 4Å, preferably more than about 8Å, more preferably equal to or greater than about 10Å and most preferably equal to or greater than about 15 Å. These intercalants containing lipophilic moieties such as hydrocarbon moieties additionally make the layer surfaces hydrophobic so intercalated layered materials are readily dried. Consequently, layers intercalated by such lipophilic materials such as hydrocarbon onium salts and hydrocarbon silanes require less high shear mixing to exfoliate in a polymer melt, to form the desired dispersion and, during melt processing, desorb less water which can cause void defects and react to break polymer chains of condensation polymers such as polyamides, polyesters, polycarbonates, and the like by hydrolysis. Such preferred intercalants produce a

polymer composite which contains a high percentage (>95%) of silicate sheets which are dispersed on a nanoscale. These composites in general display superior strength, toughness, and optical clarity.

5       The amount of swelling agent/compatibilizing agent and swelling/compatibilizing agents intercalated into swellable layered materials useful in this invention may vary substantially provided that the amount is effective to swell and, preferably to compatibilize the  
10 layers of the intercalated layered material to the extent required to provide the desired substantially uniform dispersion. In the preferred embodiments of the invention where swelling/compatibilizing agents are employed, amounts of agents employed will preferably  
15 range from about 10 mmole/100 g of layered material to about 1000 mmole/100 g of layered material. More preferred amounts are from about 20 mmole/100 g to about 200 mmole/100 g. In the case of the preferred  
20 smectite clay minerals, the more preferred amounts are from about 80 mmole/100 g to about 120 mmole/100 g of layered material.

Swellable and polymer-compatible intercalated layered material can be formed by any method. Preferably such materials are formed by intercalation  
25 of suitable agents or agents in the interlayer spaces of the swellable layered material by any suitable method. The swelling/compatibilizing agents are introduced into the interlayer spaces of the swellable layered material by any suitable method as, for  
30 example, by either insertion of neutral molecules or by ion exchange with ionic molecules, using conventional procedures. Insertion of neutral molecules may be performed by exposing finely divided layered material to intercalants in the form of a gas, neat liquid,  
35 finely divided solid, or solute in a solvent which, preferably swells the layered material. Insertion is generally aided by exposure of the mixture of

intercalant and layered material to heat, ultrasonic cavitation, or microwaves. Ion exchange by ionic molecules may be performed by suspending the layered material in a relatively volatile liquid which is

5 capable of both exfoliating and dispersing the layers of the intercalated layered material and dissolving a salt of the ionic intercalant as well as the resulting salt of the ion displaced from the layered material (e.g.,  $\text{Na}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ), adding the salt of the ionic

10 intercalant, and removing the layered material (now complexed with the new intercalant) from the liquid (now containing the dissolved salt of the displaced ion). For example, swellable layered minerals such as montmorillonite and hectorite (having primarily  $\text{Na}^+$

15 cations in the interlayer spaces) intercalate water to the point that the layers are exfoliated and dispersed uniformly in water. Dispersion in water is generally aided by mixing with relatively high shear. A suitable swelling/compatibilization agent such as the

20 hydrochloride salt of dimethyldodecylamine is then added in the desired amount after which the layers complexed with the ammonium cation are separated from the dispersion, washed of residual  $\text{NaCl}$ , and dried. In the preferred embodiments of the invention, the

25 swellable layered material is intercalated by ion exchange. For example, a suspension of a montmorillonite or a saponite in water, may be heated to about  $80^\circ\text{C}$  and stirred using a high speed homogenizer mixer, in a concentration low enough to yield a low

30 viscosity dispersion from which non-dispersible particles can be separated by sedimentation (mineral concentration of about 2% by weight, or 5% to 15% with addition of a peptizing agent such as sodium hexametaphosphate). The dispersion is combined with a

35 solution of a suitable swelling/compatibilizing agent such as an ammonium salt (as, for example the hydrochlorides of octadecylamine, 11-aminoundecanoic

acid, dioctylamine, dimethyldodecylamine, methyloctadecylamine, dimethyldidodecylamine, and the like) such that the mole ratio of ammonium salt to exchangeable ions in the mineral is between 0.5 and 5.

- 5 The amine-complexed layers may be separated from the solution by some suitable method such as filtration or centrifugation, followed by rinsing in fresh water, rough drying, and ball milling to about 100 mesh powder. The powder may be rigorously dried at 100°C to  
10 160°C in vacuum for 8 to 24 h in the presence of a drying agent such as phosphorous pentoxide, to provide the desired swellable/polymer compatible intercalated layered material.

- Intercalated layered materials intercalated with  
15 silanes may be formed by treating a swellable and polymer-compatible intercalated layered material already intercalated with an onium cation with a silane coupling agent in a swelling liquid, such as dioxane, glyme, diglyme, dimethylsulfoxide, methylethylketone,  
20 and the like, or by treating an aqueous suspension of a layered material with water-soluble silane coupling agents such as trialkoxysilanes. In the preferred embodiments, silane intercalated swellable/polymer compatible intercalated layered material is formed as  
25 follows: Onium-intercalated layered materials, preferably prepared as described above are suspended and swollen in a swelling organic liquid and treated with a trialkoxysilane. For example, montmorillonite intercalated with octadecylammonium cation, at about 80  
30 mmole of ammonium cation/100 g mineral, is combined with dioxane to form a 5% by weight suspension which is heated to 60°C and combined with a dioxane solution of aminoethylaminopropyl trimethoxysilane, such that the ratio of silane to mineral is about 20 mmole/100 g.  
35 The silane displaces the ammonium cation quantitatively to form a mixed intercalated layered material having

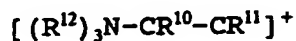
about 60 mmole of ammonium cation and 20 mmole of silane per 100 g of mineral layers.

In the preferred embodiments of this invention, swellable and polymer-compatible intercalated layered compounds include montmorillonite (Gelwhite HNF, Southern Clay Products) complexed with octdecylammonium cation (100 mmole/100 g mineral), montmorillonite complexed (Volclay, American Colloids Company) with N,N-dimethyloctadecylammonium cation (100 mmole/100 g), synthetic hectorite (Laponite S, Laporte Industries) complexed with dimethyldioctylammonium cation (80 mmole/100 g), commercially available organoclay (Claytone APA<sup>®</sup>, Southern Clay Products), montmorillonite complexed with octadecylammonium cation (about 80 mmole/g) and derivatized with aminoethylaminopropyltrimethoxysilane (20 mmole/100 g), and the like.

The amount of intercalated layered material included in the mixture may vary widely depending on the intended use of the composite. For example, relatively, larger amounts of platelet particles (exclusive of intercalant since the intercalant content in the layered material may vary), i.e. from about 15% to about 30% by wgt. of the mixture, are used in applications where articles are formed by stamping. Substantially enhanced barrier properties and heat resistance (deflection temperature under load, DTUL) are imparted by platelet particle concentrations greater than about 2.5%. Similarly, substantially enhanced strength is imparted by platelet particle concentrations greater than about 1.5%. When it is desired to preserve such properties as toughness (impact resistance) and elongation which are generally adversely affected by high loadings of any filler material including the nano-scale layered materials of this invention, it is preferred that the silicate loading be less than about 0.5%. Particle

concentration within the range 0.05 to 0.5% significantly enhance modulus, dimensional stability, and wet strength (the latter in the case of polyamides). Concentrations below 0.5% can be employed to increase melt viscosity (useful in film extrusion and in fiber melt spinning) or they may be employed in selected polymers to stabilize a particular crystalline phase (useful in the case of nylon 6 to stabilize the gamma phase) or limit spherulite size which reduces haze and increases optical clarity. In general, the amount of material employed is less than about 60% by weight of the mixture. The amount of material employed is preferably from about 0.01% to about 20 % by weight of the mixture, more preferably from about 0.05% to about 10% by weight of the mixture, and most preferably from about 0.05% to about 8% by weight.

For preferred use in forming nanocomposites, the swelling/compatibilizing agent is selected so that when subjected to the processing temperature of the matrix polymer(s), it does not evolve decomposition products which can cause chain scission or other degradation of the matrix polymers. Special care must be taken when polymers which require high processing temperatures are used. For example, quaternary ammonium cations which start to thermally decompose, at about 220 to 260°C into alkenes and amines, may be preferred for use with polyvinyl chloride, polypropylene, and nylon 6, but not for polycarbonates. On the basis of thermal stability, silanes and onium cations, that cannot undergo beta-elimination are preferred, e.g., ammonium cations of the formula:



where  $R^{10}$  is hydrogen or an organic moiety,  $R^{11}$  is an organic moiety and  $R^{12}$  is the same or different at each occurrence and is an organic radical.

The second essential ingredient of the flowable mixture is a melt processible polymer. Polymers for

use in the process of this invention may vary widely, the only requirement is that they are melt processible. As used herein, a "polymer" is a substance composed of ten or more recurring monomeric units which may be the same or different. In the preferred embodiments of the invention, the polymer includes at least thirty recurring monomeric units. The upper limit to the number of recurring monomeric units is not critical, provided that the melt index of the polymer under use conditions is such that the polymer forms a flowable mixture. More preferably, the polymer includes at least from about 30 to about 100 recurring monomeric units. In the most preferred embodiments of this invention the number of recurring units is such that the polymer has a melt index of from about 0.01 to about 12 grams per 10 minutes at the processing temperature.

Useful polymers are thermoplastic polymers or mixtures thereof, and vulcanizable and thermoplastic rubbers. Thermoplastic resins for use in the practice of this invention may vary widely. Illustrative of useful thermoplastic resins are polylactones such as poly(pivalolactone), poly(caprolactone) and the like; polyurethanes derived from reaction of diisocyanates such as 1,5-naphthalene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 2,4-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-diphenyl-methane diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 4,4'-diphenylisopropylidene diisocyanate, 3,3'-dimethyl-4,4'-diphenyl diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, dianisidine diisocyanate, tolidine diisocyanate, hexamethylene diisocyanate, 4,4'-diisocyanatodiphenylmethane and the like and linear long-chain diols such as poly(tetramethylene adipate), poly(ethylene adipate), poly(1,4-butylene

adipate), poly(ethylene succinate), poly(2,3-butylene succinate), polyether diols and the like; polycarbonates such as poly[methane bis(4-phenyl) carbonate], poly[1,1-ether bis(4-phenyl) carbonate],  
5 poly[diphenylmethane bis(4-phenyl)carbonate], poly[1,1-cyclohexane bis(4-phenyl)carbonate] and the like; polysulfones; polyether ether ketones; polyamides such as poly (4-amino butyric acid), poly(hexamethylene adipamide),  
10 poly(6-aminohexanoic acid), poly(m-xylylene adipamide), poly(p-xylylene sebacamide), poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(metaphenylene isophthalamide) (Nomex), poly(p-phenylene terephthalamide) (Kevlar), and the like; polyesters  
15 such as poly(ethylene azelate), poly(ethylene-1,5-naphthalate), poly(1,4-cyclohexane dimethylene terephthalate), poly(ethylene oxybenzoate) (A-Tell), poly(para-hydroxy benzoate) (Ekonol), poly(1,4-cyclohexylidene dimethylene terephthalate) (Kodel)  
20 (as), poly(1,4-cyclohexylidene dimethylene terephthalate) (Kodel) (trans), polyethylene terephthalate, polybutylene terephthalate and the like; poly(arylene oxides) such as poly(2,6-dimethyl-1,4-phenylene oxide), poly(2,6-diphenyl-1,4-phenylene  
25 oxide) and the like; poly(arylene sulfides) such as poly(phenylene sulfide) and the like; polyetherimides; vinyl polymers and their copolymers such as polyvinyl acetate, polyvinyl alcohol, polyvinyl chloride, polyvinyl butyral, polyvinylidene chloride, ethylene-vinyl acetate copolymers, and the like; polyacrylics,  
30 polyacrylate and their copolymers such as polyethyl acrylate, poly(n-butyl acrylate), polymethylmethacrylate, polyethyl methacrylate, poly(n-butyl methacrylate), poly(n-propyl methacrylate),  
35 polyacrylamide, polyacrylonitrile, polyacrylic acid, ethylene-acrylic acid copolymers, ethylene-vinyl alcohol copolymers acrylonitrile copolymers, methyl

methacrylate-styrene copolymers, ethylene-ethyl acrylate copolymers, methacrylated butadiene-styrene copolymers and the like; polyolefins such as low density poly(ethylene), poly(propylene), chlorinated

5 low density poly(ethylene), poly(4-methyl-1-pentene), poly(ethylene), poly(styrene), and the like; ionomers; poly(epichlorohydrins); poly(urethane) such as the polymerization product of diols such as glycerin, trimethylol-propane, 1,2,6-hexanetriol, sorbitol,

10 pentaerythritol, polyether polyols, polyester polyols and the like with a polyisocyanate such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,6-hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate and

15 the like; and polysulfones such as the reaction product of the sodium salt of 2,2-bis(4-hydroxyphenyl) propane and 4,4'-dichlorodiphenyl sulfone; furan resins such as poly(furan); cellulose ester plastics such as cellulose acetate, cellulose acetate butyrate, cellulose

20 propionate and the like; silicones such as poly(dimethyl siloxane), poly(dimethyl siloxane), poly(dimethyl siloxane co-phenylmethyl siloxane), and the like; protein plastics; and blends of two or more of the foregoing.

25 Vulcanizable and thermoplastic rubbers useful in the practice of this invention may also vary widely. Illustrative of such rubbers are brominated butyl rubber, chlorinated butyl rubber, polyurethane elastomers, fluoroelastomers, polyester elastomers,

30 butadiene/acrylonitrile elastomers, silicone elastomers, poly(butadiene), poly(isobutylene), ethylene-propylene copolymers, ethylene-propylene-diene terpolymers, sulfonated ethylene-propylene-diene terpolymers, poly(chloroprene), poly(2,3-

35 dimethylbutadiene), poly(butadiene-pentadiene), chlorosulfonated poly(ethylenes), poly(sulfide) elastomers, block copolymers, made up of segments of

glassy or crystalline blocks such as poly(styrene), poly(vinyl-toluene), poly(t-butyl styrene), polyester and the like and the elastomeric blocks such as poly(butadiene), poly(isoprene), ethylene-propylene  
5 copolymers, ethylene-butylene copolymers, polyether ester and the like as for example the copolymers in poly(styrene)-poly(butadiene)-poly(styrene) block copolymer manufactured by Shell Chemical Company under the trade name of Kraton®

10 Most preferred thermoplastic polymers are thermoplastic polymers such as polyamides, polyesters, and polymers of alpha-beta unsaturated monomers and copolymers. Polyamides which may be used in the process of the present invention are synthetic linear  
15 polycarbonamides characterized by the presence of recurring carbonamide groups as an integral part of the polymer chain which are separated from one another by at least two carbon atoms. Polyamides of this type include polymers, generally known in the art as nylons,  
20 obtained from diamines and dibasic acids having the recurring unit represented by the general formula:



in which  $\text{R}^{13}$  is an alkylene group of at least 2 carbon atoms, preferably from about 2 to about 11 or arylene  
25 having at least about 6 carbon atoms, preferably about 6 to about 17 carbon atoms; and  $\text{R}^{14}$  is selected from  $\text{R}^{13}$  and aryl groups. Also, included are copolyamides and terpolyamides obtained by known methods, for example, by condensation of hexamethylene diamine and a mixture  
30 of dibasic acids consisting of terephthalic acid and adipic acid. Polyamides of the above description are well-known in the art and include, for example, the copolyamide of 30% hexamethylene diammonium isophthalate and 70% hexamethylene diammonium adipate,  
35 poly(hexamethylene adipamide) (nylon 6,6), poly(hexamethylene sebacamide) (nylon 6, 10), poly(hexamethylene isophthalamide), poly(hexamethylene

terephthalamide), poly(heptamethylene pimelamide)  
(nylon 7,7), poly(octamethylene suberamide) (nylon  
8,8), poly(nonamethylene azelamide) (nylon 9,9) poly  
(decamethylene azelamide) (nylon 10,9),  
5 poly(decamethylene sebacamide) (nylon 10,10),  
poly[bis(4-amino cyclohexyl)methane-1,10-decane-  
carboxamide)], poly(m-xylene adipamide), poly(p-xylene  
sebacamide), poly(2,2,2-trimethyl hexamethylene  
terephthalamide), poly(piperazine sebacamide), poly(p-  
10 phenylene terephthalamide), poly(metaphenylene  
isophthalamide) and the like.

Other useful polyamides are those formed by  
polymerization of amino acids and derivatives thereof,  
as for example lactams. Illustrative of these useful  
15 polyamides are poly(4-aminobutyric acid) (nylon 4),  
poly(6-aminohexanoic acid) (nylon 6), poly(7-  
aminoheptanoic acid) (nylon 7), poly(8-aminooctanoic  
acid) (nylon 8), poly(9-aminononanoic acid) (nylon 9),  
poly(10-amino-decanoic acid) (nylon 10), poly(11-  
20 aminoundecanoic acid) (nylon 11), poly(12-  
aminododecanoic acid) (nylon 12) and the like.

Preferred polyamides for use in the practice of  
this invention are poly(caprolactam), poly(12-  
aminododecanoic acid) and poly(hexamethylene  
25 adipamide).

Other polymers which may be employed in the process  
of this invention are linear polyesters. The type of  
polyester is not critical and the particular polyesters  
chosen for use in any particular situation will depend  
30 essentially on the physical properties and features,  
i.e., tensile strength, modulus and the like, desired  
in the final form. Thus, a multiplicity of linear  
thermoplastic polyesters having wide variations in  
physical properties are suitable for use in the process  
35 of this invention.

The particular polyester chosen for use can be a  
homo-polyester or a co-polyester, or mixtures thereof

as desired. Polyesters are normally prepared by the condensation of an organic dicarboxylic acid and an organic diols, and, therefore, illustrative examples of useful polyesters will be described hereinbelow in terms of these diol and dicarboxylic acid precursors.

Polyesters which are suitable for use in this invention are those which are derived from the condensation of aromatic, cycloaliphatic, and aliphatic diols with aliphatic, aromatic and cycloaliphatic dicarboxylic acids and may be cycloaliphatic, aliphatic or aromatic polyesters.

Exemplary of useful cycloaliphatic, aliphatic and aromatic polyesters which can be utilized in the practice of their invention are poly(ethylene terephthalate), poly(cyclohexylenedimethylene terephthalate) poly(ethylene dodecate), poly(butylene terephthalate), poly[ethylene(2,7-naphthalate)], poly(methaphenylene isophthalate), poly(glycolic acid), poly(ethylene succinate), poly(ethylene adipate), poly(ethylene sebacate), poly(decamethylene azelate), poly(ethylene sebacate), poly(decamethylene adipate), poly(decamethylene sebacate), poly(dimethylpropiolactone), poly(para-hydroxybenzoate) (Ekonol), poly(ethylene oxybenzoate) (A-tell), poly(ethylene isophthalate), poly(tetramethylene terephthalate), poly(hexamethylene terephthalate), poly(decamethylene terephthalate), poly(1,4-cyclohexane dimethylene terephthalate) (trans), poly(ethylene 1,5-naphthalate), poly(ethylene 2,6-naphthalate), poly(1,4-cyclohexylidene dimethylene terephthalate), (Kodel) (cis), and poly(1,4-cyclohexylidene dimethylene terephthalate (Kodel) (trans).

Polyester compounds prepared from the condensation of a diol and an aromatic dicarboxylic acid are preferred for use in this invention. Illustrative of such useful aromatic carboxylic acids are terephthalic

acid, isophthalic acid and a o-phthalic acid, 1,3-naphthalenedicarboxylic acid, 1,4-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-diphenysulfphone-dicarboxylic acid, 1,1,3-trimethyl-5-carboxy-3-(p-carboxyphenyl)-idane, diphenyl ether 4,4'-dicarboxylic acid, bis-p(carboxy-phenyl) methane and the like. Of the aforementioned aromatic dicarboxylic acids, those based on a benzene ring (such as terephthalic acid, isophthalic acid, orthophthalic acid) are preferred for use in the practice of this invention. Amongst these preferred acid precursors, terephthalic acid is particularly preferred acid precursor.

In the most preferred embodiments of this invention, poly(ethylene terephthalate), poly(butylene terephthalate), and poly(1,4-cyclohexane dimethylene terephthalate) are the polyesters of choice. Among these polyesters of choice, poly(ethylene terephthalate) is most preferred.

Still other useful and preferred thermoplastic homopolymers and copolymers are polymers formed by polymerization of alpha-beta-unsaturated monomers or the formula:



wherein:

$R^{15}$  and  $R^{16}$  are the same or different and are cyano, phenyl, carboxy, alkylester, halo, alkyl, alkyl substituted with one or more chloro or fluoro, or hydrogen. Illustrative of such preferred homopolymers and copolymers are homopolymers and copolymers of ethylene, propylene, vinylalcohol, acrylonitrile, vinylidene chloride, salts of acrylic acid, salts of methacrylic acid, tetrafluoroethylene, chlorotrifluoroethylene, vinyl chloride and the like. Preferred are poly(propylene), propylene copolymers,

poly(ethylene) and ethylene copolymers. More preferred are poly(ethylene) and poly(propylene).

In the preferred embodiments of the invention, the polymers of choice are polymers and copolymers of  
5 olefins, polyesters, polyamides and blends thereof containing polyesters. In the particularly preferred embodiments of the invention, polymers and copolymers of ethylene, polyamides (preferably nylon 6 and nylon 66 and more preferably nylon 6), and blends thereof are  
10 used.

Some useful polymers may be naturally compatible with the underivatized layers of a layered material, such that the layered material requires only  
15 interlayer cohesive energy. These polymers include polyamides, polyesters, and other polymers having surface energies similar to that of the layers of the swellable layered materials.

The preferred polyamide useful in the preferred  
20 invention has a melt index from about 0.01 to about 10 grams/10 minutes, and preferably from 0.5 to 10 grams/10 minutes as measured by ASTM Test No. D-1238 at a load of 1000 grams at 235°C. Amongst these particularly preferred embodiments, most preferred are  
25 those embodiments in which the polyamide is nylon 6 or nylon 66, with nylon 6 being the polyamide of choice. The preferred homopolymers or copolymers of ethylene have a melt index of from about 0.01 to about 1.0 grams per 10 minutes, preferably from about 0.05 to about 0.8  
30 grams per 10 minutes as measured according to ASTM Test No. D1238 at a load of 2160 grams at 190°C.

The mixture may include various optional components which are additives commonly employed with polymers. Such optional components include nucleating agents,  
35 fillers, plasticizers, impact modifiers, chain extenders, plasticizers, colorants, mold release lubricants, antistatic agents, pigments, fire

retardants, and the like. These optional components and appropriate amounts are well known to those of skill in the art, accordingly, only the preferred optional components will be described herein in detail.

5 In the second step of the process of this invention, the flowable mixture is subjected to a shear having an "effective shear rate". As used herein, an "effective shear rate" is a shear rate [as shear rate is defined in Ferdinand Rodriguez, "Principles of  
10 Polymers Systems", McGraw-Hill Book Company, New York (1982)] which is effective to delaminate at least about 90% by weight of the intercalated material to form platelet particles described above, and provide a composition comprising a polymeric matrix having  
15 platelet particles substantially homogeneously dispersed therein. In the preferred embodiments of the invention, the shear rate is greater than about  $10 \text{ sec}^{-1}$ . In these preferred embodiments of the invention, the upper limit for the shear rate is not critical  
20 provided that the shear rate is not so high as to physically degrade the polymer. In the particularly preferred embodiments of the invention, the shear rate is from greater than about  $10 \text{ sec}^{-1}$  to about  $20,000 \text{ sec}^{-1}$ , and in the most preferred embodiments of the invention  
25 the shear rate is from about  $100 \text{ sec}^{-1}$  to about  $10,000 \text{ sec}^{-1}$ .

Any method which can be used to apply a shear to a flowable mixture or any polymer melt can be used. The shearing action can be provided by any appropriate  
30 method, as for example by mechanical means, by thermal shock, by pressure alteration, or by ultrasonics. Methods useful in shearing melts are known in the art, and will not be described in great detail. In particularly useful procedures, the flowable polymer  
35 mixture is sheared by mechanical methods in which portions of the melt are caused to flow past other portions of the mixture by use of mechanical means such

as stirrers, Banbury® type mixers, Brabender® type mixers, long continuous mixers, and extrudes. Another procedure employs thermal shock in which shearing is achieved by alternatively raising or lowering the temperature of the mixture causing thermal expansions and resulting in internal stresses which cause the shear. In still other procedures, shear is achieved by sudden pressure changes in pressure alteration methods; by ultrasonic techniques in which cavitation or resonant vibrations which cause portions of the mixture to vibrate or to be excited at different phases and thus subjected to shear. These methods of shearing flowable polymer mixtures and polymer melts are merely representative of useful methods, and any method known in the art for shearing flowable polymer mixtures and polymer melts may be used.

In the preferred embodiments of the invention, mechanical shearing methods are employed such as by extrusion, injection molding machines, Banbury® type mixers, Brabender® type mixers and the like. In the more preferred embodiments of the invention, shearing is achieved by introducing the polymer melt at one end of the extruder (single or double screw) and receiving the sheared polymer at the other end of the extruder. The temperature of the polymer melt, the length of the extruder, residence time of the melt in the extruder and the design of the extruder (single screw, twin screw, number of flights per unit length, channel depth, flight clearance, mixing zone etc.) are several variables which control the amount of shear to be applied.

Upon subjecting a flowable mixture of said swellable intercalated layered material and said polymer melt to shear mixing, at least about 80% by weight, preferably at least about 85% by weight, more preferably at least about 90% by weight and most preferably at least about 95% by weight of the layers

of the material delaminate to form platelet particles substantially homogeneously dispersed in the polymer matrix. As used herein, "platelet particles" are particles having two relatively flat opposite faces wherein the thickness of which is the distance between the faces, which is relatively small compared to the size of the faces. As formed by this process, the platelet particles dispersed in matrix polymers have the thickness of the individual layers, or small multiples less than about 10, preferably less than about 5 and more preferably less than about 3 of the layers, and still more preferably 1 or 2 layers. In the preferred embodiments of this invention, intercalation of every interlayer space is complete so that all or substantially all individual layers delaminate one from the other to form separate platelet particles. In cases where intercalation is incomplete between some layers, those layers will not delaminate in the polymer melt, and will form platelet particles comprising those layers in a coplanar aggregate. These latter platelet particles still constitute nanoscale and nanodispersed fillers and provide enhanced properties over and above those provided by conventional micro-scale fillers, as long as they are less than about 10 layers thick and preferably less than 5 layers thick. The other dimensions of the platelet particles may vary greatly, but in the case of particles derived from clay minerals, the particle faces are roughly round or oblong having average diameters between about 10,000 Å and about 50 Å, such that the aspect ratio length/thickness ranges from about 1000 to about 1. For the purposes of the present invention, the average diameter is defined as the diameter of a circle having an area equal to the surface area of one broad surface face of the platelet shaped particle. The average diameter is determined from particle surface area as measured with a Leitz

Texture Analyzer System in a fully computerized and automated mode. In the preferred embodiments of the invention the average thickness of the platelet particles is equal to or less than about 20 Å and the average diameter is between 5,000 Å and 100 Å. Most preferably the average thickness is about 10 Å. The most preferred average diameter depends on both the desired property of the nanocomposite and the ease of complete intercalation and delamination to form the nanocomposite structure. High aspect ratios, and therefore large average diameters, are generally preferred for reinforcement and barrier properties, while layered materials having smaller platelets are preferred for their ease of delamination. Thus, for purposes of the nanocomposite properties, the most preferred average diameter is greater than about 150 Å, and, for purposes of delamination, it is less than about 3000 Å.

The average interparticle spacing between delaminated layers may vary widely after shearings, depending on the concentration of layered material. In general the higher the concentration of layered material in the polymer matrix particle the smaller the interparticle spacing; and conversely, the lower the concentration of layered material, the larger the interparticle spacing. In general, interparticle spacing is equal to or greater than 15Å. The interparticle spacing is preferably equal to or greater than about 20Å more preferably equal to or greater than about 30Å and most preferably equal to or greater than about 50Å.

As used herein "uniformly dispersed" is defined as a degree of dispersion of the platelet shaped particles having a standard deviation in platelet particle density, down to a sampling volume of  $10^{-15} \text{m}^3$ , which is preferably less than about 50% of the mean, more preferably less than about 30% of the mean, and most

preferably less than about 20% of the mean as determined from estimates based on transmission electron microscopy.

The process of this invention is preferably carried out in the absence of air, as for example in the presence of an inert gas, such as, argon, neon, nitrogen or the like. The process can be carried out in a batchwise or discontinuous fashion, as for example, carrying out the process in a sealed container. Alternatively, the process can be carried out in a continuous fashion in a single processing zone, as for example by use of an extruder, from which air is largely excluded, or in a plurality of such reaction zones in series or parallel.

The nanocomposites of this invention exhibit useful properties which are superior to those predicted by U.S. Patent Nos. 4,739,007 and 5,810,734. Various useful performance indices can be devised in order to jointly assess different performance aspects using a single number. Depending upon the nature of the devised index, comparisons can be made either between samples containing the same loading of layered material or the index can be more broadly applied to polymers having different loadings of clay. For example, the effect of adding nanoscale particulate fillers dispersed platelet particles to a polymer typically increases tensile modulus and ultimate tensile strength while decreasing ultimate elongation. In the case where combinations of high modulus ( $Y$ ) and high ultimate elongation ( $\Delta L/L$ ) are required, a useful performance index for comparing samples with similar particulate loading is  $Y(\Delta L/L)$ . Likewise, when tensile strength ( $S$ ) combined with high ultimate elongation is sought, a useful performance index for comparing samples with similar loading levels is  $S(\Delta L/L)$ . The preferred embodiments of the present invention provide a  $Y(\Delta L/L)$  of above about 660 MPa (preferably equal to

or greater than about 800 MPa more preferably equal to or greater than about 1000 MPa and most preferably equal to or greater than about 1200 MPa) for a loading of about 2% of nanodispersed layered material such as montmorillonite in a melt processible polymer such as nylon 6. In contrast, the prior art patents on in-reactor nanocomposite blends (U.S. 4,739,007 and U.S. 4,810,734) provide a maximum  $Y(\Delta L/L)$  of about 660 MPa. Also, preferred embodiments of the present invention provide a  $S(\Delta L/L)$  of above about 20 MPa (preferably equal to or greater than about 25 MPa and more preferably equal to or greater than about 30 MPa) for a loading of about 2% intercalated layered material such as montmorillonite, while the maximum value for this figure of merit obtained in the above mentioned in-reactor process patents is about 20 MPa at 2% loading. While we do not wish to be bound by any theory, it is believed that the unique properties of the nanocomposites of this invention result from the use of swelling/compatibilizing agents which do not react to become part of the main chain of the matrix polymer (as do the swelling agents preferred in the prior art U.S. 4,739,007 and U.S. 4,810,734) when used in the in-reactor processes. Instead, the preferred swelling/compatibilizing agents of this invention, which remain bonded to the particle surface, interact with the matrix polymer in one or more of the following ways: (1) covalent bond formation to form branches on the main chains of the matrix polymer, (2) hydrogen, ion-dipole, and dipole-dipole bonding with portions of the matrix polymer, and (3) Van der Waals attraction and entanglement with the matrix polymer. Nanocomposites having particularly attractive combinations of modulus, tensile strength and ultimate elongation are formed using swelling/compatibilizing agents, under category (3) above, which are bonded to the particle surface, and whose polymer-interacting

moiety projects away from the particle surface and is only weakly bonded to the matrix polymer. This function is best performed by silane compounds and onium compounds (especially ammonium compounds) of the type having a lipophilic moiety such that the surface tension, at 20°C, of the derivatized particle is between about 55 and 15 dyne/cm, and preferably between 45 and 20 dyne/cm, as determined by measuring the contact angles made by sessile drops of liquids on the solid surfaces. Illustrative of these preferred silane compounds and onium are silanes of the formula; - $\text{Si}(\text{R}^9)_2\text{R}^8$  and ammonium cations of the formula: - $\text{NH}(\text{R}^{17})_2\text{R}^{18}$  and  $-\text{N}(\text{R}^{17})_3\text{R}^{18}$  where  $\text{R}^9$  is the same or different at each occurrence and is alkyl, alkoxy or oxysilane;  $\text{R}^{17}$  is the same or different at each occurrence and is alkyl and  $\text{R}^{18}$  and  $\text{R}^8$  are the same or different and are organic groups which are compatible with the polymer. Preferably,  $\text{R}^{18}$  and  $\text{R}^8$  are groups such that the silane compound or ammonium radical on the particle has a surface tension at 20°C of less than about 55 dyne/cm. The surface tension of platelet particles derivatized with agents containing octadecane moieties is estimated to be about 31 to about 38 dyne/cm by analogy to poly(ethylene) and poly(propylene). In contrast, the surface tension of 11-aminoundecanoic acid is estimated to be about 59 dyne/cm by analogy to poly(ethylene-co-acrylic acid) (20 mole % acrylic acid) (Polymer Handbook, Third Edition, J. Brandrup and E.H. Immergut, eds. (Wiley, New York, 1989) pp. VI411).

The nanocomposite compositions according to the invention are thermoplastic and, in some cases, vulcanizable materials from which molded articles of manufacture having valuable properties can be produced by conventional shaping processes, such as melt spinning, casting, vacuum molding, sheet molding, injection molding and extruding. Examples of such

molded articles are components for technical equipment, apparatus castings, household equipment, sports equipment, bottles, containers, components for the electrical and electronics industries, car components, circuits, fibers, semi-finished products which can be shaped by machining and the like. The use of the materials for coating articles by means of powder coating processes is also possible, as is their use as hot-melt adhesives. The molding compositions according to the invention are outstandingly suitable for specific applications of all types since their spectrum of properties can be modified in the desired direction in manifold ways. Such molded products of this invention will derive one or more advantages over products molded with polymers having no nanodispersed platelet particles including increased modulus, stiffness, wet strength, dimensional stability, and heat deflection temperature, and decreased moisture absorption, flammability, permeability, and molding cycle time.

The molding compositions according to the invention are outstandingly suitable for the production of sheets and panels having valuable properties. Such sheets and panels may be shaped by conventional processes such as vacuum processing or by hot pressing to form useful objects. The sheets and panels according to the invention are also suitable as coating materials for other materials comprising, for example, wood, glass, ceramic, metal or other plastics, and outstanding strengths can be achieved using conventional adhesion promoters, for example, those based on vinyl resins. The sheets and panels can also be laminated with other plastic films and this is preferably effected by co-extrusion, the sheets being bonded in the molten state. The surfaces of the sheets and panels, including those in the embossed form, can be improved or finished by

conventional methods, for example by lacquering or by the application of protective films.

The compositions of this invention are especially useful for fabrication of extruded films and film  
5 laminates, as for example, films for use in food packaging. Such films can be fabricated using conventional film extrusion techniques. The films are preferably from about 10 to about 100 microns, more preferably from about 20 to about 100 microns and most  
10 preferably from about 25 to about 75 microns in thickness. In the film, the major plane of the platelet fillers is substantially parallel to the major plane of the film. The extent of parallelism of particles and film can be determined by X-ray analysis.  
15 X-ray analysis is a useful way to described the crystallinity and orientation of polymer crystals and the orientation of platelet particles. A convenient method of X-ray analysis is that described in Hernans, P.H. and Weidinger A., Makromol Chemie, Vol. 44, pp.  
20 24-36 (1961), hereby incorporated by reference.

For the purpose of the present invention Op, the platelet orientation factor, is an indication of the platelet particle orientation in the film. The Op was determined by making azimuthal scans from densitometer  
25 tracings of the X-ray photographs which were obtained by exposing the edge of the film to the incident X-rays. The angle is the angle between the reference direction, the normal to the film, and the normal to the plane of interest, the major plane of the platelet.  
30 The Op values were calculated as the average cosine square ( $\langle \cos^2 \rangle$ ) for the normal to the flat faces of the platelet particles. An Op of 1.0 indicates that the faces of the platelets are completely parallel to the plane of the film. An Op of 0.0 indicates that the  
35 faces of the platelets are perpendicular to the plane of the film. The Op of the platelets in the film of the present invention is preferably from about 0.70 to

about 1.0, more preferably from about 0.90 to about 1.0 and most preferably from about 0.95 to about 1.0. Such preferred orientation of platelet particles results in enhanced barrier properties and increased tare  
5 strength.

The homogeneously distributed platelet particles and polymer are formed into a film by suitable film-forming methods. Typically, the composition is melted and forced through a film forming die. The die can be  
10 a flat die or a circular die. A typical flat die is a hanger shaped die, and a typical circular die is a tubular film die.

The film of the nanocomposite of the present invention may go through steps to cause the platelets  
15 to be further oriented so the major planes through the platelets are substantially parallel to the major plane through the film. A method to do this is to biaxially stretch the film. For example, the film is stretched in the axial or machine direction by tension rollers  
20 pulling the film as it is extruded from the die. The film is simultaneously stretched in the transverse direction by clamping the edges of the film and drawing them apart. Alternatively, the film is stretched in the transverse direction by using a tubular film die  
25 and blowing the film up as it passes from the tubular film die. The films of this invention may exhibit one or more of the following benefits: increased modulus, wet strength, and dimensional stability, and decreased moisture adsorption and permeability to gases such as  
30 oxygen and liquids such as water, alcohols and other solvents.

The following specific examples are presented to more particularly illustrate the invention and are not to be construed as limitations thereon.

EXAMPLE 1

Three nylon 6/montmorillonite nanocomposites, each comprising about 2% by weight montmorillonite layers, were prepared by extruding nylon 6 along with powdered montmorillonite intercalated with cations derived from 11-aminoundecanoic acid (Mont-11), octadecylamine (Mont-18), and a tertiary alkylamine (in a commercial intercalated montmorillonite, Claytone APA™, obtained from Southern Clay Products). The octadecylamine-montmorillonite complex (Mont-18) was prepared by combining a water/ethanol solution of octadecylamine hydrochloride with a hot (60 to 80°C) aqueous dispersion of montmorillonite such that the ratio of ethanol to water in the dispersion was about 10% by volume. The stoichiometry of the mixture was 0.11 moles of amine per 100 g of mineral, or 1.1 equivalents of the mineral's ion exchange capacity. The octadecylamine hydrochloride solution was prepared by dissolving the amine in hot ethanol and combining this solution with hot water containing a 20% excess of hydrochloric acid. The aqueous dispersion of montmorillonite was prepared by stirring montmorillonite (Gelwhite HNF™, Southern Clay Products) into hot water (60-80°C) for 30 min using a homogenizer, adding 5 g of a peptizing agent (sodium hexametaphosphate) per 100 g of mineral, and separating out non-dispersible particles by sedimentation. The Mont-18 complex formed a precipitate which, after standing 16 h, was filtered, washed 5 times with hot water, dried in a fluid bed dryer, ball milled to 100 mesh, and rigorously dried in vacuum at 130°C in the presence of phosphorus pentoxide for 16 h. The 11-aminoundecanoic acid-montmorillonite complex was formed by a similar procedure. Claytone APA was dried in vacuum at 130°C prior to compounding.

The nanocomposite of the octadecylamine-montmorillonite complex (Mont 18) in nylon 6 was formed

by feeding a mixture of nylon 6 pellets and rigorously dried octadecylamine-montmorillonite complex into a twinscrew extruder (Leistritz) equipped with general purpose screws and a vacuum attached to the die for devolatilization of the melt. Extruder heaters and screw speed were adjusted to settings used for processing the homopolymer. The nylon 6 nanocomposites of the 11-aminoundecanoic acid-montmorillonite (Mont-11) and Claytone APA were formed using a similar procedure.

Films were formed from the nanocomposites by extrusion through a die. The films were evaluated for light transmission. The extrudate transmitted light without haze or distortion.

The nanocomposite extrudates was dried and injection molded into test bars and the tensile strength and tensile modulus determined by the procedure of ASTM D638. The tensile strength and tensile modulus of the nylon was also evaluated for comparison purposes. The results are set forth Table 1. Tensile bars of nylon 6 homopolymer and each of the nanocomposites were immersed in water at 20°C for 14 days and their tensile properties evaluated. These results are set forth in the following Table 2.

**TABLE 1**

<b>TENSILE PROPERTIES OF NYLON 6/MONTMORILLONITE NANOCOMPOSITES DRY AS MOLDED</b>				
5	<b>Composite</b>	<b>Tensile Strength, psi (MPa)</b>	<b>Tensile Modulus, psi (MPa)</b>	<b>Elongation %</b>
	Nylon 6	11,000 (76)	366,000 (2,530)	>200%
	1.6% montmorillonite (aminoundecanoic acid)	13,300 (92)	415,000 (2,870)	5%
	1.7% montmorillonite (- octadecylamine)	13,200 (91)	440,000 (3,040)	25%
	2.0% montmorillonite (Claytone APA)	13,300 (92)	544,000 (3,760)	36%
10	a. percentage is weight % mineral in the composite as determined from the ash content.			
15	b. based on formic acid viscosities corrected for the contribution of the dispersed silicates to the measured viscosities.			
20				

TABLE 2

5	TENSILE PROPERTIES OF NYLON 6/MONTMORILLONITE COMPOSITES (1/8" TENSILE BARS) TESTED AFTER 14 DAYS IN WATER AT 20c			
	Composite	Tensile Strength, psi (MPa)	Tensile Modulus, psi (MPa)	Elongation %
	Nylon 6	4,200 (76)	113,000 (780)	>100%
	1.6% montmorillonite (-aminoundecanoic acid)	6,000 (41)	185,000 (1,280)	60%
10	1.7% montmorillonite (-octadecylamine)	6,200 (43)	206,000 (1,420)	>100%
15	2.0% montmorillonite (Claytone APA)	6,200 (43)	220,000 (1,520)	>100%

Both dry-as-molded and water-soaked nanocomposite tensile test bars exhibited tensile strength and modulus superior to those of the extruded nylon. Table 1 shows that the average elongation-at-break of the two alkylammonium cation-intercalated montmorillonite nanocomposites, those with montmorillonite intercalated with octadecylammonium cation and the quaternary ammonium cation used in Claytone APA were superior to a comparable nanocomposite of 11-aminoundecanoic acid-montmorillonite complex.

EXAMPLE 2

A series of experiments were carried out to evaluate the effect of varying the concentration of intercalated montmorillonite (intercalated with 11-aminoundecanoic acid cation, Mont-11) on the properties of the nylon 6 nanocomposites. In these experiments, a series of nylon 6/Mont-11 nanocomposites, comprising montmorillonite layers in amounts ranging from 0.26% to 8.1% by weight, were prepared by extruding nylon-6 pellets along with powdered Mont-11. Comparison samples of homopolymer and a 9.3% composite of untreated montmorillonite were extruded as well. The Mont-11 complex was prepared and processed according to

the procedures described in Example 1, except for the following changes. An aqueous solution of 11-aminoundecanoic acid hydrochloride was combined with a 2% dispersion of montmorillonite. The more highly loaded composites (the 8.1% nanocomposite and the 9.3% composite of untreated montmorillonite) were prepared by adding an appropriate amount of the mineral component downstream in the extruder into already melted polymer. All samples were injection molded into test bars. The flexural strength and flexural modulus of the samples were evaluated by the procedures of ASTM D790, and their heat deflection temperatures, under 264 psi of load (DTUL 264), were evaluated by the procedures of ASTM D648. The results are set forth in Table 3.

TABLE 3

Composition	Flexural Strength, psi (MPa)	Flexural Modulus, psi (MPa)	Deflection Temperature at 264 psi (C)
nylon 6	15,500 (107)	385,000 (2,660)	55.6
0.27% silicate <sup>a</sup>	15,700 (108)	426,000 (2,940)	58.4
0.89% silicate	19,000 (131)	437,000 (3,020)	60.0
4.12% silicate	19,200 (133)	620,000 (4,280)	109.3
8.10% silicate	19,600 (135)	650,000 (4,490)	127.4
9.25% clay, unintercalated <sup>b</sup>	19,000 (131)	496,700 (3430)	59.2

- a. montmorillonite intercalated by 11-aminoundecanoic acid cation (dispersible in polymer melt).  
 b. montmorillonite intercalated by Na<sup>+</sup> cation (non-dispersible in polymer melt).

As shown in Table 2, test bars of the nanocomposites exhibited enhanced flexural modulus over the homopolymer at loadings as low as 0.26% and enhanced flexural strength at loadings as low as 0.89%.

Using dynamic mechanical analysis, the effect of temperature on the elastic modulus of the nanocomposites was evaluated. The results are set forth in FIGs 1 and 2. As shown in FIG 1, the various nanocomposites showed comparable enhancements in their elastic modulus values at room temperature, but this enhancement increased substantially at temperatures above the glass transition temperature  $T_g$  (ca.  $75^\circ\text{C}$ ). The composite of untreated montmorillonite exhibited greater strength and stiffness than the homopolymer, but not as great as the comparably loaded nanocomposite. As shown in FIG 2, the difference in elastic modulus values between the comparably loaded composites is particularly great at temperature above the  $T_g$ .

The average polymer molecular weight of in the nanocomposites declined with increased loading of the aminoundecanoic acid-montmorillonite complex, presumably due to chain scission reactions between the polyamide and the complex. Reactions with water or amines desorbed from the complex appeared to be, at most, a minor contributor to chain scission, since thermogravimetric analysis of the complex indicated no significant weight loss up to the melt processing temperature (ca.  $260^\circ\text{C}$ ) that might be attributed to these species. By elimination, reaction with the carboxylic acid portion of the 11-aminoundecanoic acid cation appeared to be the most likely contributor to chain scission. In this case, omega-amino acids appear to be not preferred for use in melt processing mineral complexes with condensation polymers such as polyamides, polyesters, polycarbonates, and the like.

Films of nylon 6/Mont-11 nanocomposites were compression molded and evaluated for their water vapor and oxygen transmissions rates at both 0% and 100% relative humidity, using the procedures of ASTM D3985. The results are set forth in the following table 4.

**Table 4**  
**GAS TRANSMISSION RATES**

Composition	WVTR <sup>a</sup>	OTR <sup>b</sup> at 0% Relative Humidity	OTR <sup>b</sup> at 100% Relative Humidity <sup>b</sup>
nylon 6	20	3.0	14.3
0.47% silicate	-	-	11.0
1.55% silicate	-	-	8.1
4.12% silicate	4	0.78	7.5

a. water vapor transmission rate (g-mil/100in<sup>2</sup>/day)

b. oxygen transmission rate (cc-mil/100in<sup>2</sup>/day)

As shown in Table 4, relative to nylon 6, the water vapor transmission rate decreased by a factor of 5 and the oxygen transmission rate (at 0% relative humidity) decreased by a factor of about 4 in films having about 4% by weight platelet particles dispersed in the nylon and oriented by the molding process with the planes of the particles substantially parallel with the plane of the film. Under the plasticizing influence of 100% relative humidity, the oxygen transmission rate was decreased by a factor of 1.8 at 1.55 weight % particles, and by a factor of 1.9 at 4.12 weight % particles.

### EXAMPLE 3

A series of experiments were carried out to compare various properties of nanocomposites formed by melt blending and by in-reactor compounding. Two comparable nanocomposites of nylon 6 were prepared: one by melt processing, and the other by in-reactor compounding. Both were injection molded into test bars which were characterized dry-as-molded.

The former, a 4.1% Bentonite nanocomposite, was formed by extruding powdered Bentonite intercalated with 11-aminoundecanoic acid cation with nylon 6 pellets on a

single screw Killion extruder. The complex was prepared as described in Example 2.

The latter, a 4.5% bentonite nanocomposite, was prepared by polymerizing caprolactam in the presence of the bentonite-11-aminoundecanoic acid complex and aminocaproic acid (1%, by weight). The reaction mixture was stirred at 255°C in a steel resin kettle equipped with an "anchor" type stirrer. After 2.5 h, the polymerization mixture was cooled, ground into particles (ca. 2 mm in diameter), and washed 3 times, for 1 h each time, in boiling water. The washed composite was dried, extruded and pelletized, and redried.

The two nanocomposites were qualitatively the same in most respects: x-ray diffraction (XRD) patterns, infrared (IR) spectra, melting and crystallization temperatures (DSC), optical microscopy, transmission electron microscopy (TEM), and mechanical properties. Analysis of the XRD patterns indicated that both composites were about 50% crystalline, had crystallite coherence lengths of 70Å to 80Å. This crystalline portion was 80% to 90% in the gamma phase of nylon 6. IR confirmed the predominance of gamma phase and indicated a higher concentration of silicate in the in-reactor composite. Optical microscopy showed that, in both composites, large spherulites were prevented from forming. TEM's of each composites showed parallel streaks (presumed to be edge views of the layers) that were less than 200Å thick and 300Å to 1500Å long. The TEM of the extruder-formed nanocomposite is shown in FIG 3. The tensile modulus, yield strength, and heat deflection temperature under load (DTUL 264 psi) were determined by the procedures of ASTM D638 and D648, respectively. The results are set forth in Table 5.

**TABLE 5**

NYLON 6/BENTONITE NANOCOMPOSITES BY MELT MIXING and MONOMER BLENDING AND POLYMERIZING PROCESSES (dry as molded)			
Composition	Tensile Modulus, psi (MPa)	Yield Strength <sup>a</sup> , psi (MPa)	DTUL <sup>b</sup> @ 264 psi (C)
Nylon 6	380,000 (2,630)	10,300 (71)	57
melt-mixed <sup>c</sup> Nylon 6/ bentonite 4.1% silicate	610,000 (4,210)	13,400 (93)	109
in-reactor nylon 6/bentonite 4.5% silicate	580,000 (4,010)	13,400 (93)	129
a. composites broke at or before yield; elongation was ca. 10%.			
b. heat deflection temperature under load.			
c. single screw extruder.			

The results show that the tensile modulus and yield strength values of the two composites were nearly identical, while the heat deflection temperature of the in-reactor composite was 20°C higher. We speculate that the difference in DTUL values reflected less complete exfoliation and dispersion in the polymer melt-mixed nanocomposite.

**Example 4**

Nanocomposites of the mont-11 complex were prepared by extrusion with nylon 10-10, nylon 6,6-6 (6:4), and an amorphous polyamide, nylon 6,6-6,6-10. The compositions were fabricated into test bars and the flexural strength, flexural modulus and elongation-to-break were evaluated as described in Example 1. The results set forth in Tables 6, 7 and 8. In each case, the composite exhibited enhanced mechanicals over the homopolymer.

**TABLE 6**

Composition	Flexural Strength, psi (MPa)	Flexural Modulus, psi (MPa)	elongation at break (%)
Nylon 10,10	9,200 (64)	290,500 (2,010)	250
2% montmorillonite <sup>a</sup>	11,000 (76)	370,500 (2,560)	20

5

**Table 7**

Composition	Flexural Strength, psi (MPa)	Flexural Modulus, psi (MPa)	Elongation at break (%)
Nylon 6,66	14,000 (97)	330,000 (2,280)	230
2% montmorillonite <sup>a</sup>	16,500 (114)	400,000 (2,760)	>80
(a) Treated with 11' aminoundecanoic acid HCl			

10

15

**Table 8**

Composition	Tensile Strength (psi) (MPa)	Tensile Modulus (psi) (MPa)	Elongation at Break %
Nylon 6,6-6,6-10	5,700 (39)	205,000 (1,420)	>200
1% montmorillonite <sup>a</sup>	6,800 (47)	275,000 (1,900)	>200
a. Treated with 11-aminoundecanoic acid HCl.			

**EXAMPLE 5**

A molding grade of nylon 6 (Grade 8202 obtained from Allied-Signal) was compounded with montmorillonite intercalated with octadecylammonium cation as described in Example 1. It was also compounded with two different loading of silanized wollastonite particles for purposes of comparison. 96% of the wollastonite, a needle-like mineral, was comprised of particles of less than 10 microns in length, and it was silanized with aminopropyl trimethoxysilane. The composites were injection molded into test samples and evaluated for their flexural properties and heat deflection temperatures under 264 psi of load. The results are set forth in Table 9.

**TABLE 9**

Composition	Flexural Modulus, psi (MPa)	Flexural Strength, psi (MPa)	DTUL 264 psi (C)
8% wollastonite <sup>a</sup>	464,000 (3,210)	18,100 (125)	59.2
16% wollastonite <sup>a</sup>	515,700 (3,560)	19,800 (137)	68.7
6% dispersed silicate <sup>b</sup>	630,000 (4,350)	21,100 (146)	126.9

a. silanized with aminopropyltrimethoxysilane.

b. from montmorillonite intercalated with octadecylammonium cation, Mont-18.

**EXAMPLE 6**

Two nanocomposites of non-polyamides were formed by feeding a mixture of intercalated montmorillonite and

polymer pellets into a twinscrew extruder. One composite was polyethyleneterephthalate, PET, having 0.36% mineral derived from Claytone APA. The other was polypropylene having 0.14% mineral derived from Mont-18. Both composites were injection molded into test samples and evaluated for their tensile properties. The results are set forth in Tables 10 and 11. Both composites exhibited increases in stiffness and strength over their homopolymers, even at these low loadings.

**TABLE 10**

Composition	Tensile Modulus, psi (MPa)	Yield Strength, psi (MPa)
PET <sup>a</sup>	270,000 (1,870)	7,900 (55)
PET/0.38% montmorillonite <sup>b</sup>	314,000 (2,170)	8,100 (56)

a. poly(ethylene terephthalate)

b. derived from montmorillonite intercalated with octadecylammonium cation.

**TABLE 11**

Composition	Tensile Modulus, psi (MPa)	Yield Strength, psi (MPa)
polypropylene	220,000 (1,520)	4,900 (34)
polypropylene/0.14% montmorillonite <sup>a</sup>	243,000 (1,680)	5,200 (36)

a. derived from Claytone APA.

**EXAMPLE 7**

Nanocomposites of montmorillonite, derivatized with silanes, and nylon 6 were formed by extruding nylon pellets along with silane derivatized montmorillonite following the procedure of Example 1. Silane-derivatized montmorillonite was prepared by adding the silane to a dispersion of Claytone APA in refluxing dioxane (100 g Claytone per 1000 mL dioxane) in a ratio of 70 mmole of silane per 100 g of silicate in the Claytone. The

derivatized silicate was separated by filtration from the dioxane and the displaced amine species. The silanes used were aminoethylaminopropyl(trimethoxy)silane and trimethoxysilyloctadecane. The tensile modulus, yield strength, and ultimate elongation of the nanocomposites were determined by the procedures of ASTM D638. The results are set forth in the following Table 12.

**TABLE 12**

Composition	Tensile Modulus psi (MPa)	Tensile Strength psi(MPa)	Elongation at Break (%)
nylon <sup>6</sup> control	422,700 (2,920)	11,000 (76)	36
2.66 % silicate aminoalkylsilane	530,400 (3,660)	12,100 (83)	10
1.05 % silicate octadecylsilane	559,300 (3,860)	12,600 (87)	45

The combination of tensile properties exhibited by the composite of octadecylsilane-derivatized silicate compares favorably with that of similarly loaded nanocomposites of montmorillonite derivatized by 11-ammoniumundecanoic acid cation, octadecylammonium cation, and the quaternary ammonium cation in Claytone, as shown in Table 1. In addition, it unexpectedly exhibits an increase in elongation compared to the homopolymer as well as the reinforcement characteristic of the nanocomposites.

**EXAMPLE 8**

Nanocomposites of montmorillonite, derivatized by a silane coupling agent, with polypropylene are prepared by treating mont-18 with vinyltris(t-butylperoxy)silane (3.2 g silane per 123 g mont-18), drying the resulting compound at 130°C for 6 h, and compounding the resulting powder with polypropylene melt in an extruder. The resulting nanocomposite exhibits enhanced mechanical

properties over nanocomposites having no silane treatment.

EXAMPLE 9

A nanocomposite of montmorillonite and nylon 6,  
5 having 5.14% silicate by weight and having a particularly  
high modulus, was formed by extruding Claytone APA with  
nylon 6 pellets following the procedure in Example 1.  
The tensile modulus was 727,000 psi (5,020 MPa) which  
constituted a 72% increase over that of the homopolymer  
10 (422,700 psi(2,920 MPa)).

WHAT IS CLAIMED IS:

1. Composite material comprising a melt processible polymer matrix and dispersed platelet particles having average thicknesses less than 50 Å, and having chemical species bonded to them, said chemical species having a moiety which projects away from the particle surface and which is not covalently bonded to the polymer matrix, said platelet particles being present in an amount less than about 60% by weight of the composite material wherein the chemical species is selected from the group consisting of chemical species comprising a silane function or onium cation function and having a group which is compatible with the matrix polymer.

2. Composite material as defined in claim 1, wherein the chemical species is selected from silanes of the formula:  $(-\text{Si}(\text{R}^9)_2\text{R}^8)$  and ammonium cations of the formula:  $(-\text{NH}_2\text{R}^{18})$ ,  $(-\text{NH}_2\text{R}^{17}\text{R}^{18})$ ,  $(-\text{NH}(\text{R}^{17})_2\text{R}^{18})$  and  $(-\text{N}(\text{R}^{17})_3\text{R}^{18})$ , where  $\text{R}^9$  is the same or different at each occurrence and is alkyl, alkoxy, or oxysilane,  $\text{R}^{17}$  is the same or different at each occurrence and is alkyl, and  $\text{R}^8$  and  $\text{R}^{18}$  are the same or different and groups which are compatible with the matrix polymer.

3. Composite material as defined in claim 1, wherein said matrix polymer is a thermoplastic polymer selected from the group consisting of polyamides, polyesters, polycarbonates, celluloses, phenolics, poly(urethanes), poly(sulfones), poly(etheretherketones), poly(esteramides), poly(phenylenesulfides), poly(amideimides), polyacetals, poly(alkylene oxides), poly(phenylene oxides), poly(imides) and polymers formed by the polymerization of alpha, beta-unsaturated monomers of the formula:  $\text{R}^{15}\text{R}^{16}-\text{C}=\text{CH}_2$ , wherein  $\text{R}^{15}$  and  $\text{R}^{16}$  are the same or different and are hydrogen, hydroxy, halo, alkylcarbonyl, carboxy, alkoxycarbonyl, heterocycle, alkyl or aryl either unsubstituted or substituted with one or more substituents selected from the group consisting of alkoxy, cyano, hydroxy, alkyl, and aryl.

4. Composite material as defined in claim 2, wherein  $R^8$  and  $R^{18}$  are the same or different and are moieties selected from a group consisting of alkyl, cycloalkenyl, cycloalkyl, aryl, or alkylaryl, either unsubstituted or  
5 substituted with amino, alkylamino, dialkylamino, nitro, azido, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, alkyl, aryloxy, arylalkylamino, alkylamino, arylamino, dialkylamino, diarylamino, aryl, alkylsulfinyl, aryloxy, alkylsulfinyl, alkylsulfonyl,  
10 arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, alkylsilane, and a moiety of the formula:



wherein  $R^6$  is alkyl, cycloalkyl, aryl,  $R^1$  is hydrogen, alkyl, or aryl, and Z is -O- or -NR<sup>7</sup>-, where  $R^7$  is  
15 hydrogen, alkyl, aryl, or alkylsilane.

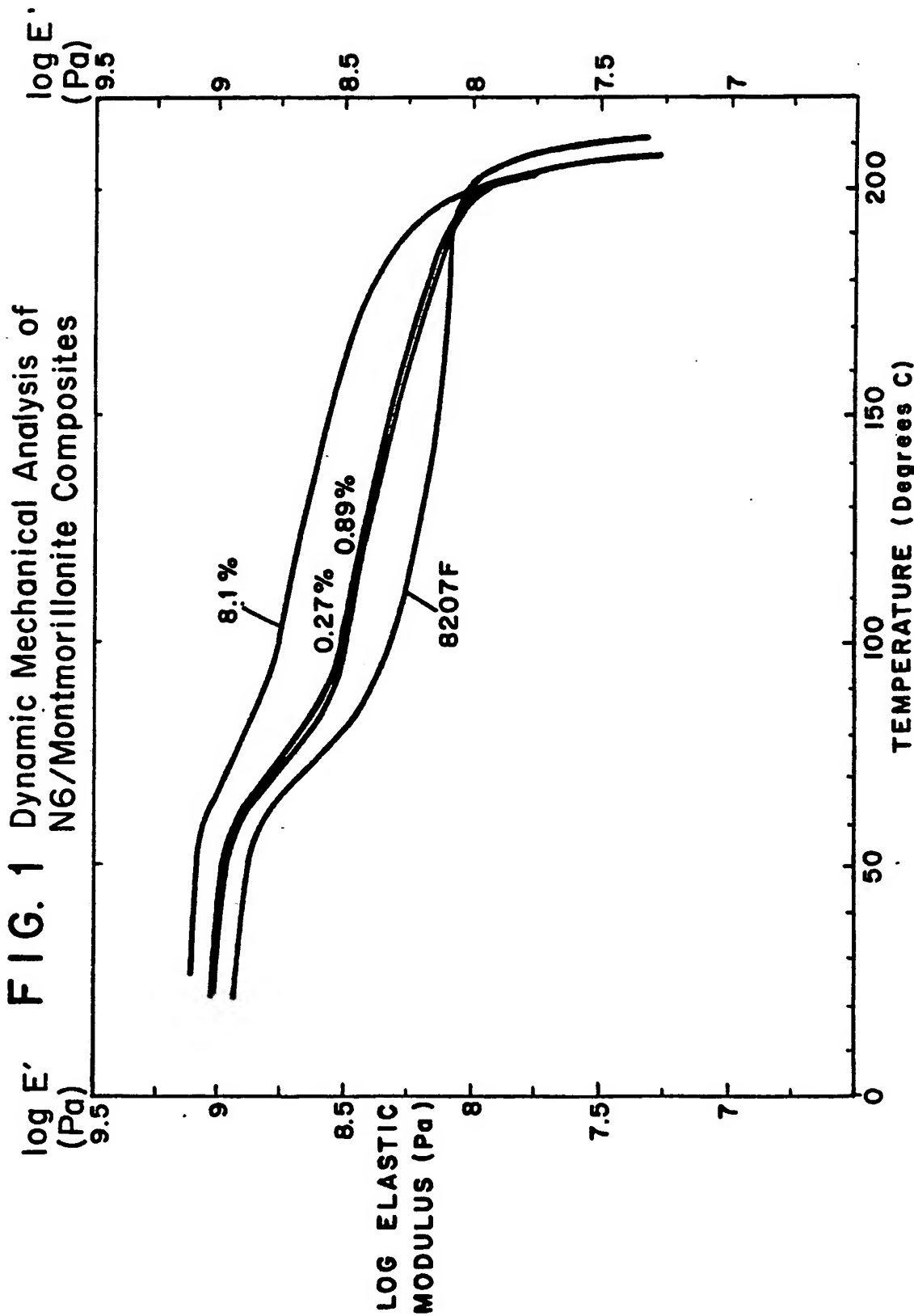
5. Composite material of claim 1 wherein said platelet particle is less than 50 Å thick.

6. Composite material of claim 5, wherein said platelet particle is between 20 Å and 7 Å in thickness.

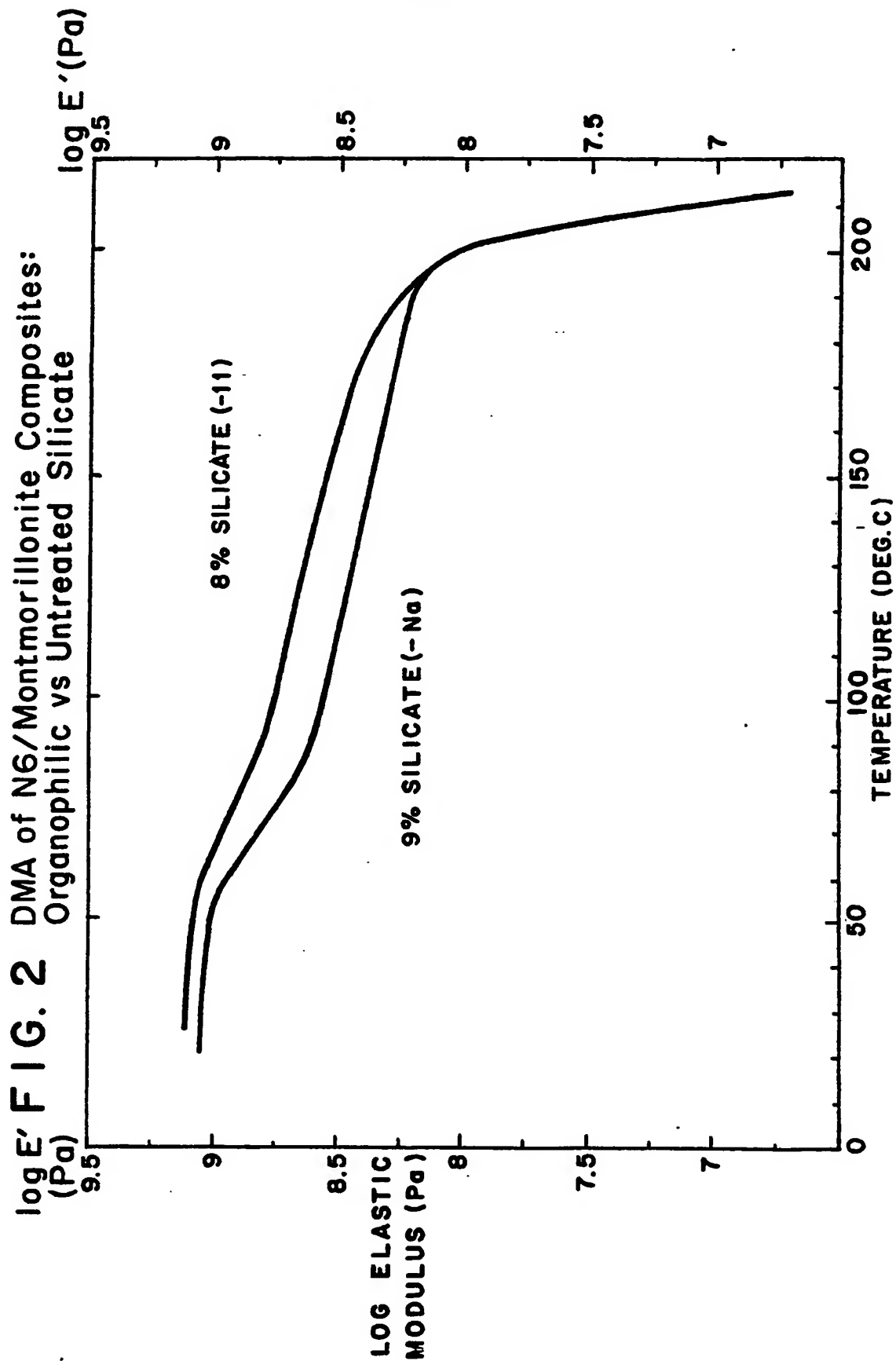
20 7. Composite material of claim 1 wherein the interparticle spacing between platelet particles is greater than about 15 Å.

8. Composite material of claim 1 wherein said platelet particle is a phyllosilicate.

25 9. An article of manufacture comprising a body, said body fabricated, totally or in part, from a composite material comprising a melt processible polymer matrix and dispersed platelet particles having average thicknesses less than 50 Å and a maximum thickness of 100 Å, and  
30 having chemical species bonded to them, said chemical species having a moiety which projects away from the particle surface and which is not covalently bonded to the polymer matrix, said platelet particles being present in an amount less than about 60% by weight of the  
35 composite material.



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**FIGURE 3**  
**4% MONTMORILLONITE in NYLON**



## INTERNATIONAL SEARCH REPORT

PCT/US 92/06733

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08K9/04; C08K9/06		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C08K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP,A,0 398 551 (UBE INDUSTRIES, LTD.) 22 November 1990 see claims; examples 1,2	1-6,8,9
X	EP,A,0 276 915 (IMPERIAL CHEMICAL INDUSTRIES PLC) 3 August 1988 see claims; examples	1-6,8,9
X	GB,A,2 048 285 (GENERAL ELECTRIC COMPANY) 10 December 1980 see page 2, line 29 - line 32; claims 1,10,11; examples 1-4	1-4,8,9
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
30 NOVEMBER 1992	- 8. 12. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	FUHR C.K.B.	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. US 9206733  
SA 63807**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 30/11/92

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